Sensitivities of Ozone and Fine Particulate Matter Formation to Emissions under the Impact of Potential Future Climate Change

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Impact of climate change alone and in combination with currently planned emission control strategies are investigated to quantify effectiveness in decreasing regional ozone and $PM_{2.5}$ over the continental U.S. using MM5, SMOKE, and CMAQ with DDM-3D. Sensitivities of ozone and $PM_{2.5}$ formation to precursor emissions are found to change only slightly in response to climate change. In many cases, mass per ton sensitivities to NO_x and SO_2 controls are predicted to be greater in the future due to both the lower emissions as well as climate, suggesting that current control strategies based on reducing such emissions will continue to be effective in decreasing ground-level ozone and $PM_{2.5}$ concentrations. SO_2 emission controls are predicted to be most beneficial for decreasing summertime $PM_{2.5}$ levels, whereas controls of NO_x emissions are effective in winter. Spatial distributions of sensitivities are also found to be only slightly affected assuming no changes in land-use. Contributions of biogenic VOC emissions to $PM_{2.5}$ formation are simulated to be more important in the future because of higher temperatures, higher biogenic emissions, and lower anthropogenic NO_x and SO_2 emissions.

Introduction

Climate change is forecast to affect ambient temperatures, precipitation frequency, and stagnation conditions (*1*, *2*), all of which impact regional air quality. Increases in ground-level ozone concentrations are expected in the future due to higher temperatures and more frequent stagnation events (*3*–*6*). Ozone-related health effects are also anticipated to be more significant (*7*). Prior work suggests $PM_{2.5}$ (particulate matter with aerodynamic diameter less than 2.5 μm) levels will increase in some areas but not in others, largely due to changes in precipitation (*8*). Both ozone and $PM_{2.5}$ are also found to impact climate via direct and indirect effects on radiative forcing (*9*). An issue of primary importance for policymakers is how well currently planned control strategies for improving air quality for ozone and $PM_{2.5}$ that are based on the current climate will work under future global climate change scenarios. This can be investigated by quantifying sensitivities of air pollutants e.g., ozone and $PM_{2.5}$ to their precursors e.g., nitrogen oxides ($NO_x = NO + NO_2$), volatile organic compounds (VOCs), ammonia (NH_3), and sulfur dioxide (SO_2) under both historic and potential future climatic conditions.

Sillman et al. (*10*) and Milford et al. (*11*) present sensitivities of ozone formation to its precursors, NO_x and VOCs. They identified the factors that affect sensitivity of ozone to NO_x and VOCs including the ratio of VOC to NO_x concentrations, reactivity of VOCs, abundance of biogenic hydrocarbons, photochemical aging, and rates of meteorological dispersion (*12*). Ambient particulate matter formation, including inorganic components (e.g., ammonium, nitrate, and sulfate) and secondary organic aerosols (SOA), are found to be influenced by ambient temperature, humidity, clouds, and precursor concentrations (*13*–*16*). Both anthropogenic and biogenic VOCs contribute to SOA (*17, 18*), though biogenic VOCs are thought to be more important on a global scale (*19, 20*). Since higher ambient temperatures lead to higher biogenic VOC emissions as a result of climate change (assuming no changes in vegetation coverage) (*21, 22*), future climate-induced emission changes are expected to alter how ozone and PM formation will respond to their precursor emissions (i.e., sensitivities) even if anthropogenic emissions do not change significantly. Recent studies suggest that ozone concentrations are more sensitive to precursor emission changes from controls than to climate-induced effects (*23*). If the same is true for $PM_{2.5}$, this would suggest that current emphasis on local and regional controls should continue to provide air quality benefits.

Responses of future ozone and $PM_{2.5}$ levels to both climate change and to emission changes are quantified using historic (years of 2000–2002) and projected future (years of 2049–2051) meteorology. The target future period from 2049 to 2051 is chosen as a compromise between being far enough in the future to experience nontrivial climate modification, yet is still within a reasonable horizon for air quality planning. If the pollutant fields and their sensitivities to anthropogenic emissions in the future are similar to current conditions, the conclusion would be that climate considerations will not significantly impact design of current control strategies that deal with ozone and $PM_{2.5}$ as much as if the relative sensitivities changed markedly. If the sensitivities are similar, but the pollutant levels are significantly different, then control strategies should focus on degree of controls rather than direction. If, however, the sensitivities are significantly different, future control decisions should consider how climate change might be addressed in formulating strategies along with associated uncertainties. This work extends the previous work by Tagaris et al. (*8*) to show the sensitivities of different air pollutants to emissions which provides critical information for the air pollution control strategies.

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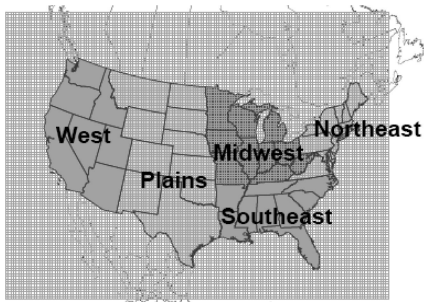

FIGURE 1. Simulation domain with 111 × 147 horizontal grid cells which being 36 by 36 km and the U.S. regions–west, plains, midwest, northeast, and southeast.

Materials and Methods

Details of the modeling approach are given in Tagaris et al. (*8*), and summarized here. The fifth-generation NCAR/Penn State Mesoscale Model (MM5) (*24, 25*) is used to downscale NASA's Goddard Institute of Space Studies (GISS) (*26*) global climate model results for years of 2000–2002 and 2049–2051 (*4, 6*). Meteorological model evaluation has been presented by Tagaris et al. and Leung and Gustafson (*4*). Emissions for Canada, Mexico, and the U.S. for 2000–2002 are processed using the Sparse Matrix Operator Kernel Emissions (SMOKE) modeling system (www.cep.unc.edu/empd/EDSS/emissions). For future emissions, we use forecasts accounting for reductions in NO_x, SO_2 and VOC corresponding to current regulations in the U.S., Canada, and Mexico (which include reductions from the Clean Air Interstate Rule (CAIR) controls (*27*)) up to 2020. From 2020 to 2050, we use forecasts from the Integrated Model to Assess the Global Environment (IMAGE) model (www.mnp.nl/image), based on IPCC A1B scenario (see Woo et al. for details (*28*)).

The community multiscale air quality model (CMAQ) (*29*) with SAPRC-99 (*30*) chemical mechanism and decoupled direct method 3D (DDM-3D) (*31–34*) are used to simulate historic and future ozone and $PM_{2.5}$ concentrations, and to quantify their sensitivities to specific sets of emissions; including both anthropogenic and biogenic VOC emissions, anthropogenic NO_x, total NH_3, and total SO_2, over a domain covering the United States as well as parts of Canada and Mexico. A uniform grid of 36 by 36 km horizontal cells with nine vertical layers is employed (Figure 1). DDM-3D directly calculates the first-order local sensitivities of both gas- (*35*) and condensed-phase (*36*) pollutants to precursor emissions, i.e., the first-order sensitivity ($S_{i,j}$) of pollutant concentration i (C_i) to source emissions j (E_j) is calculated as follows:

$$S_{i,j} = E_j \frac{\partial C_i}{\partial E_j} \tag{1}$$

The first-order (linearized) sensitivities, as presented here, have the same units as the corresponding pollutants. These sensitivities represent how pollutant concentrations would respond to a 100% reduction in precursor emissions if the systems were linear, which is typically reasonable for reductions of 25–50% emissions, depending on pollutant and environment (*35*).

In this work, two different future scenarios are studied. First, the changes in sensitivities due to the impact of potential future climate change alone are examined by using historic and potential future climates, but keeping future emissions source strengths the same as in historic episodes ("non-projected" or "np" scenario). In the second scenario, potential future meteorological fields and expected future emissions, projected following the IPCC mid-level increase scenario, A1B emission scenario (*37*), and recent regulatory actions (*27*), are applied in the regional air quality simulations. Simulations performed in this study are summarized in Table 1. By comparing the results of sensitivity analyses from different scenarios, contributions of ozone and $PM_{2.5}$ precursors and effectiveness of control strategies are quantified.

Simulations using nonprojected (np) emissions in the future (i.e., 2050_np and 2049–2051_np summers in Table 1) use the same emission inventories as 2001 but the emissions are not identical as some components of emissions (e.g., biogenic VOC and mobile source NO_x) have been adjusted to respond to future climate/meteorology (Table S2 in the Supporting Information (SI)).

Results and Discussion

Regional variations are found by dividing the continental U.S. into five large regions: west, plains, midwest, northeast, and southeast (Figure 1) taking into account different characteristics of precursor emissions and air pollutant formation processes. Sensitivity results are presented by averaging over the continental U.S. and each region separately for the year 2001, summers (June, July, and August) of 2000–2002, the year 2050, and summers of 2049–2051 with both projected and nonprojected emissions. Additionally, the first-order sensitivities of the 2050 scenario are also normalized by 2050 emissions and multiplied by 2001 emissions to compare the sensitivities of ozone and $PM_{2.5}$ formation with the 2001 scenario based on "per unit" (e.g., per ton) of precursor emissions ("2050_Norm").

$$S_{2050\_Norm} = S_{2050} \frac{E_{2001}}{E_{2050}} \tag{2}$$

Details of meteorology- and emission-simulation results are given elsewhere (*4, 8, 28*) and are summarized here. Annual average surface temperatures are predicted to increase by about 0–3 K over the simulation domain between 2001 and 2050. The higher temperatures in 2050 are accompanied by increases in absolute humidity in most of the domain (up to 20% compared to 2001). For emissions, SO_2 and NO_x emissions are forecast to be reduced 51% each between 2001 and 2050, largely due to current regulations being fully implemented. NH_3 emissions are predicted to rise in the future (~7%) from increases in population and related activities (*8, 28*). If the effects of increased activities and planned emission controls are not considered, SO_2 (+4%) and NO_x (+2%) emissions change only slightly due to temperature dependent processes (e.g., microbial activities, increased exhaust emissions). Without controls of future anthropogenic emissions, VOC emissions are predicted to increase (+15%) due to warmer climate along with temperature-sensitive emissions from biogenic and mobile sources and other evaporative processes. On the other hand, with controls, anthropogenic VOC emissions are predicted to decrease in the future, offsetting increases in biogenic VOC emissions. Combined effects of those two mechanisms cause total VOC (i.e., anthropogenic and biogenic VOCs) emissions to increase approximately 2% (SI, Table S2).

Ozone Sensitivities. To quantify how ozone levels will continue to respond to controls, CMAQ with DDM-3D was used to calculate ozone sensitivities to biogenic VOCs, anthropogenic VOCs, and anthropogenic NO_x emissions for the historic and future periods with and without controls. Simulated 2001/2050 yearly and 2000–2002/2049–2051 summer fourth-highest daily maximum 8 h average ozone (4th MDA8 h ozone) is calculated for comparison to EPA's National Ambient Air Quality Standards (NAAQS). Results of sensitivities of annual and summertime (JJA) fourth MDA8 h ozone to precursor emissions are then averaged by regions as well as for the continental U.S. (Figure 2). First-order (linearized) sensitivities suggest each 10% reduction in anthropogenic NO_x emissions causes ~2−4% decreases in fourth MDA8 h

TABLE 1. Summary of Air Quality Simulations

scenario	emission inventory (E.I.)	climatic conditions	future air quality impacting factors
2001	historic (2001)	historic (2001 complete year)	N.A.[a]
2000–2002 summers	historic (2000–2002)	historic (2000–2002 summers[b])	N.A.
2050_np[c]	historic (2001)	future (2050 complete year)	potential future climate changes
2049–2051_np_summers	historic (2000–2002)	future (2049–2051 summers[b])	potential future climate changes
2050	future (2050)	future (2050 complete year)	potential future climate changes and emission controls
2049–2051 summers	future (2049–2051)	future (2049–2051 summers[b])	potential future climate changes and emission controls

[a] N.A., not applicable. [b] Summers include June, July, and August. [c] "np" means no projection in emission inventories. Emission inventories for 2049–2051 are the same as 2000–2002.

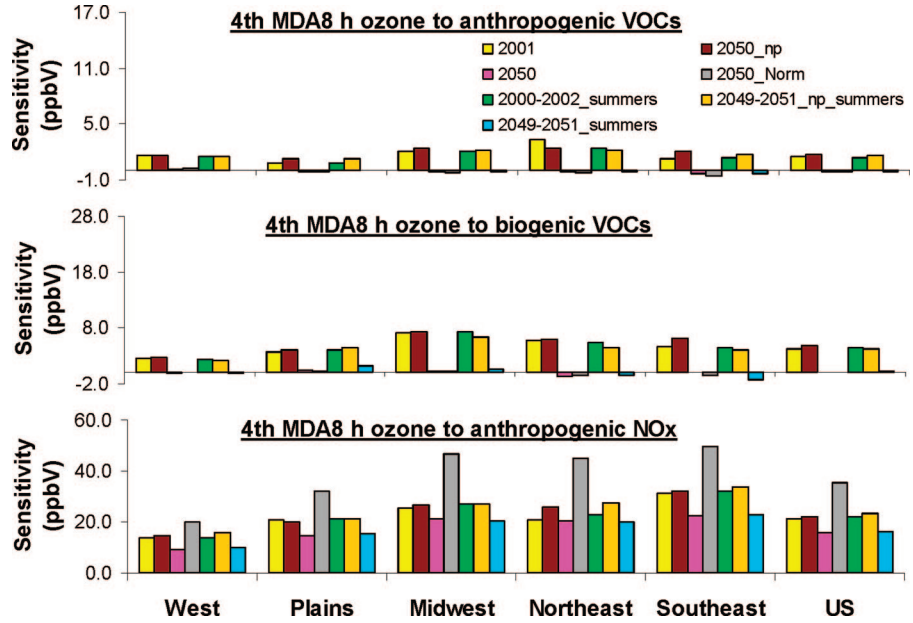

FIGURE 2. Sensitivities of annual and summertime (JJA) 4th MDA8 h O_3 to domain-wide emissions of biogenic and anthropogenic VOCs and anthropogenic NO_x for the five regions and U.S. (note the change in scales).

O_3 concentrations in both 2001 and 2050 when emission controls are not included (SI, Table S1) on a regional basis. Reductions in VOC emissions are also beneficial for decreasing ozone levels for historic and future episodes without projected emission controls. Overall, ozone and its relative sensitivities to anthropogenic NO_x, biogenic VOC, and anthropogenic VOC emissions are predicted to increase only slightly in 2050 without considering emission controls as compared to 2001.

For scenarios with projected emissions ("2050" and "2049–2051 summers"), future reductions in anthropogenic precursor emissions decrease the total contributions of anthropogenic NO_x and anthropogenic/biogenic VOCs to ozone formation because of the 51% reduction in NO_x emissions. However, sensitivities of ozone formation to "per unit" (e.g., ton) NO_x emission ("2050_Norm" in Figure 2) increase significantly because the reductions in NO_x and steady VOC emissions shift ozone formation toward being more NO_x-limited. Conversely, sensitivities of ozone formation to per unit emissions of anthropogenic and biogenic VOCs are both lower in 2050 as compared to 2001. Changes in multisummer sensitivities of fourth MDA8 h ozone formation to precursor emissions between different scenarios (2000–2002_summers, 2049–2051_np_summers, and 2049–2051_summers) are found to be in good agreement with the changes in yearly simulations (Figure 2). If one looks at regional variations in all subregions, sensitivities of fourth MDA8 h ozone formation to anthropogenic NO_x emissions are highest in the southeast because of greater biogenic VOC emissions. Year-to-year variations in sensitivities of fourth MDA8 h ozone to anthropogenic NO_x emissions during summers are found to be small for 2000–2002 and 2049–2051 with both projected and nonprojected emissions (Table 2). Such results suggest more consecutive yearly simulations are not expected to significantly change interpretation of sensitivity analysis.

Spatial distributions of sensitivities of annual fourth MDA8 h ozone to anthropogenic NO_x emissions for the scenarios of 2001, 2050_np, and 2050 are found to be similar, though the magnitudes of sensitivities of 2001 and 2050_np are higher than 2050 due to controls of anthropogenic NO_x emissions and associated decreases in ozone concentrations in the future (Figure 3a–c). On the other hand, planned future emission controls are predicted to shift ozone formation to being more NO_x-limited in 2050 over the simulation domain. This suggests that reductions in anthropogenic NO_x emissions will continue to be effective for reducing regional ozone concentrations, even more so than is currently the case.

$PM_{2.5}$ Sensitivitie. Sensitivities of 2050 annual average speciated $PM_{2.5}$ formation to its precursors are predicted to be similar to 2001 when nonprojected emission inventories are simulated ("2050_np") (Figure 4), even though climate change influences $PM_{2.5}$ formation in several ways. First, changes in temperatures shift the partitioning of volatile and semivolatile compounds between gas and condensed phases. Higher temperatures favor condensable compounds existing

TABLE 2. Sensitivities of Summertime (JJA) 4th MDA8 h Ozone To Domain-Wide Anthropogenic No_X Emission for the Five Regions and the Continental U.S.

unit: ppbV

	2000	2001	2002	2049_np	2050_np	2051_np	2049	2050	2051
west	13.4	14.4	13.3	15.2	15.2	17.5	9.5	9.8	10.6
plains	21.4	21.6	21.2	21.9	19.5	22.3	15.7	15.2	15.7
midwest	27.6	25.4	27.7	24.8	24.6	32.3	18.4	19.5	22.9
northeast	24.6	21.1	23.1	24.7	26.4	31.2	17.8	19.5	22.2
southeast	33.8	31.4	31.5	34.3	31.5	35.8	23.3	22.3	23.4
U.S.	22.6	22.0	22.1	22.8	21.6	25.5	16.0	16.0	17.4

as gases, thus decreasing the mass of condensed material. This is true for nitrate and secondary organic aerosols. Increases in absolute humidity due to higher temperature can increase OH concentrations in the atmosphere. Since OH radicals are strong oxidants, higher OH concentrations are expected to favor more rapid oxidation of SO_2 and NO_x, forming condensable compounds in the atmosphere. Most notable effects, however, relate to meteorological processes affecting dispersion (e.g., stagnation periods) and loss (e.g., wet deposition due to rain). Surprisingly, the net effects of those mechanisms cause only slight changes in $PM_{2.5}$ (see Tagaris et al.,2007) and their sensitivities (Figure 4).

Relative sensitivities of sulfate fraction of $PM_{2.5}$ to SO_2 emissions (SO4_SO2) and nitrate of $PM_{2.5}$ to anthropogenic NO_x emissions (NO3_ANOX) ("A" presents "anthropogenic") are predicted to decrease with projected emissions in 2050 due to reductions in emissions (Figure 4). However, sensitivities of nitrate aerosol formation per unit NO_x emission increase, although the contribution of per unit SO_2 emission to sulfate aerosol does not change significantly ("2050_Norm"). The increase in sensitivity of nitrate aerosol formation to per unit NO_x emission is due to both higher projected ammonia emissions and reductions in SO_2 emissions which make more NH_3 available to react with nitric acid to form ammonium nitrate. Sensitivities of sulfate $PM_{2.5}$ formation to ammonia (SO4_NH3) are predicted to increase due to higher, future ammonia emissions. Higher ammonia/ammonium concentrations tend to neutralize cloudwater, allowing more rapid SO_2 oxidation by ozone. On the other hand, lower NO_x emissions decrease ammonium nitrate formation in the nitrate-limited environment and reduce sensitivities of nitrate $PM_{2.5}$ to NH_3 emissions (NO3_NH3). Overall, changes in sulfate and nitrate lead to less ammonium $PM_{2.5}$ formation

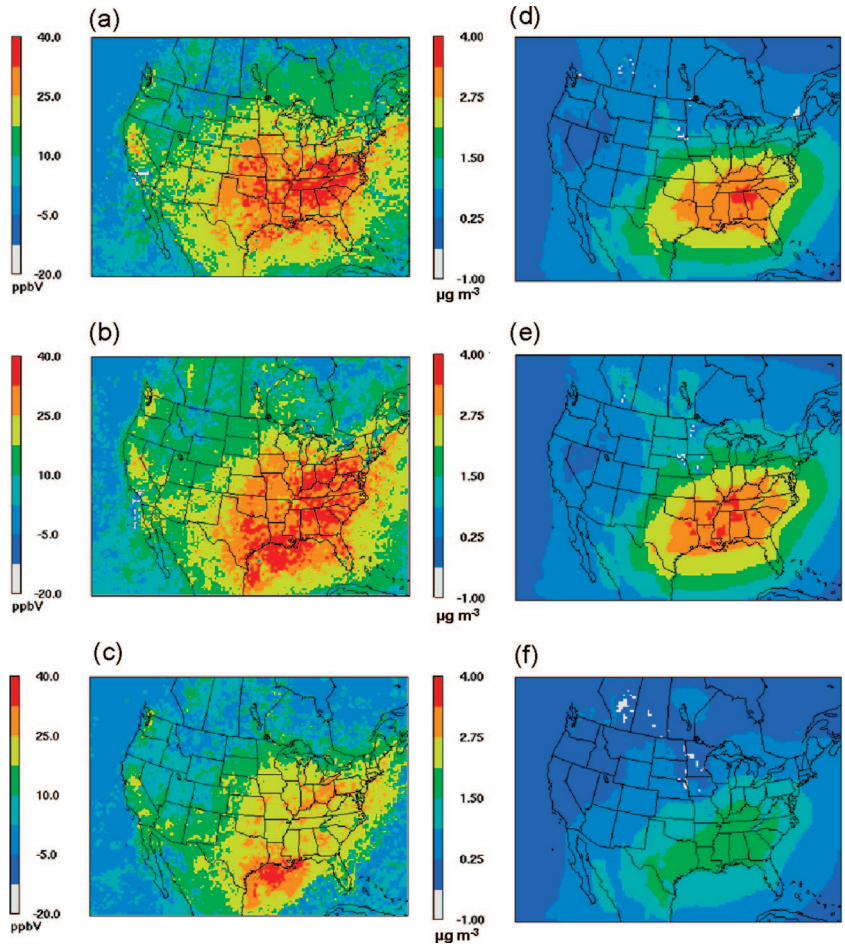

FIGURE 3. Spatial distribution of sensitivities of annual 4th MDA8 h ozone to domain-wide anthropogenic NO_x emissions (a, b, and c), and annual averaged sensitivities of $PM_{2.5}$ formation to domain-wide SO_2 emissions (d, e, and f) for 2001, 2050_np, and 2050 (top to bottom) (sensitivities presented here are first-order sensitivities).

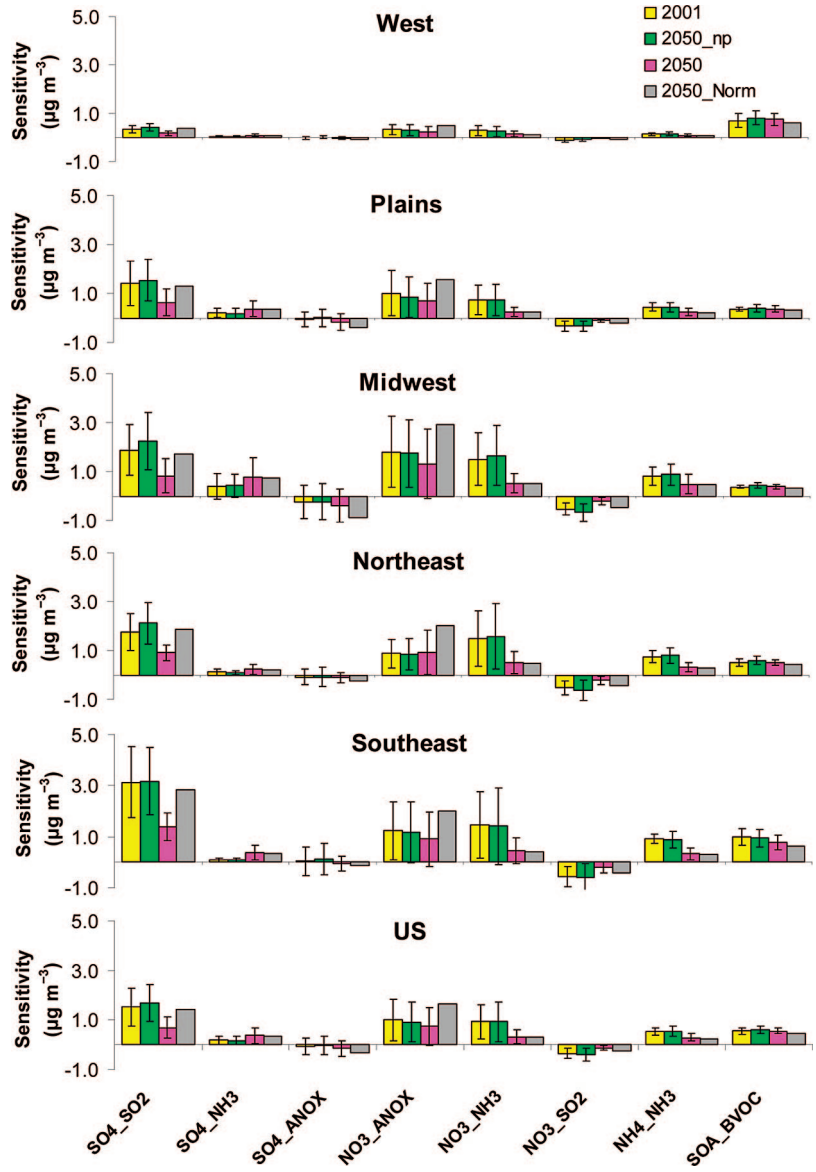

FIGURE 4. Sensitivities of speciated $PM_{2.5}$ formation to domain-wide precursor emissions for the scenarios of "2001", "2050", "2050_np", and "2050_Norm" (error bars represent standard deviations of month-to-month variability of sensitivities).

TABLE 3. Single- and Three-Summer Average Sensitivities of $PM_{2.5}$ to Domain-Wide SO_2 Emissions

unit: $\mu g\ m^{-3}$

	single-summer average			three-summer average		
	2001	2050_np	2050	2000–2002	2049–2051_np	2049–2051
west	0.58	0.57	0.29	0.58	0.56	0.28
plains	2.90	2.81	1.64	2.96	2.47	1.42
midwest	3.60	3.88	2.03	4.10	3.51	1.84
northeast	2.44	3.32	1.47	2.83	2.85	1.29
southeast	5.15	5.51	2.72	5.73	4.80	2.36
U.S.	2.77	2.90	1.54	3.00	2.57	1.35

and decrease sensitivities of ammonium $PM_{2.5}$ to ammonia emissions (NH4_NH3).

SO_2 emission reductions lead to increases in nitrate aerosol formation (NO3_SO2 is negative), whereas anthropogenic NO_x emission reductions have small impacts on sulfate aerosol formation (SO4_ANOX). Decreases in SO_2 emissions make more ammonia/ammonium available for ammonium nitrate formation, though a small increase in nitrate is simulated. Similarly, lower NO_x emissions decrease nitrate aerosol, slightly increasing sulfate, which arises from a decreased atmospheric acidity, increases heterogeneous sulfate formation. Thus, the net effects of SO_2 and NO_x reductions are predicted to decrease $PM_{2.5}$ mass under both current and potential future climate conditions. Unlike high ozone levels and their sensitivities, which are consistently observed in the summer, temporal variations, presented by standard deviation of month-to-month variability, of sensitivities of speciated $PM_{2.5}$ are found in a yearly simulation (Figure 4). $PM_{2.5}$ sensitivities with the largest variabilities are SO4_SO2, NO3_ANOX, and NO3_NH3 (SI Figure S1). Sen-

sitivities of sulfate $PM_{2.5}$ to SO_2 emissions are simulated to be more important during summers than other seasons, whereas sensitivities of nitrate to NO_x and NH_3 emissions are found being the highest in the winter (SI Figure S1). This is true because NH_4NO_3 has higher vapor pressure and is more sensitive to high temperatures than $(NH_4)_2SO_4$. Gilliland et al. present an underestimation of NH_3 emissions in summers and overestimation in winters since seasonal variations of NH_3 emissions are not included in current inventories (*38*). Therefore, seasonal trends of NH_4NO_3 and $(NH_4)_2SO_4$ are expected to be more significant if seasonal variation in NH_3 emissions are considered. Those results show that SO_2 emissions dominate $PM_{2.5}$ formation in the summer, whereas emissions of SO_2, NO_x and NH_3 are all comparably important for decreasing secondary $PM_{2.5}$ levels in the winter. Seasonal variability of sensitivity of secondary organic aerosol (SOA) to biogenic VOC emissions (SOA_BVOC) ("B" presents "biogenic") was also found due to higher biogenic VOC emissions and faster oxidation of VOCs in summers. Increases in sensitivity of sulfate to SO_2 in the summer are due to an increased photochemical oxidation and stagnation. On the other hand, high temperatures decrease particle-phase ammonium nitrate condensation in summers but the converse is true at other times. Differences in single- and three-summer average (e.g., 2001 vs 2000–2002) sensitivities of $PM_{2.5}$ to SO_2 emissions are found to be small (up to ~16%) for 2000–2002 and 2049–2051 with both projected and nonprojected emissions (Table 3). Spatial distributions of sensitivities of total $PM_{2.5}$ formation to SO_2 emissions in 2050 with both projected and nonprojected emissions are also examined and found to be similar to 2001 (Figure 3d−f), showing that the conversion of SO_2 to sulfate is only slightly sensitive to climate change. The sensitivity reduction found in some areas is due to precipitation (*39*).

Contributions of biogenic VOC emissions to $PM_{2.5}$ formation are simulated to be more important in the future because of higher temperatures, resulting in higher biogenic VOC emissions whereas future emission reductions due to planned controls decrease the sensitivities of $PM_{2.5}$ formation to SO_2 and NO_x emissions (Figure 4). However, SO_2, NH_3, anthropogenic NO_x and biogenic VOCs are still found to continue to be important precursors for $PM_{2.5}$ formation in the future with both projected and nonprojected emissions. These results also suggest that $PM_{2.5}$ formation is only slightly sensitive to the simulated climate change with the direction of impact ambiguous, and planned controls of SO_2 and NO_x emissions will continue to be effective in reducing $PM_{2.5}$ concentrations in the future. Climate-induced changes can slightly increase control effectiveness in some locations ("2050_np" and "2049–2050_np_summers" in Figures 2 and 4). For ozone and $PM_{2.5}$, the impact of emission controls has a greater effect on sensitivities than simulated climate change between 2001 and 2050.

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Supporting Information Available

Additional information is available in two tables and one figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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